

# Factors influencing precision when measuring natural samples using ICP-MS

Brian Alexander



# Instrument Details

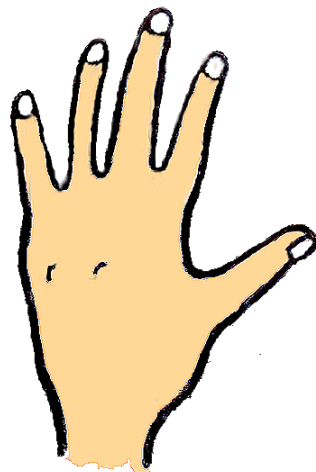
- Quadrupole ICP-MS
- Standard introduction system
  - Scott style spray chamber
  - Cross-flow nebulizer
  - Peristaltic pump
- No collision/reaction cell analysis



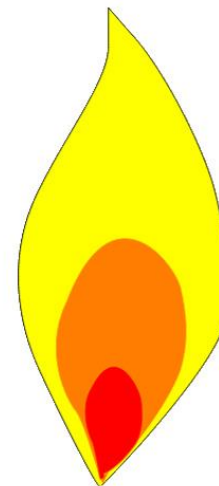
# Possible Factors Influencing Precision



Sample



Person



Machine

# Sample Types

## All samples are reference materials

- Basalt (oceanic crust) = 50%  $\text{SiO}_2$ ; Al-, Fe-, Mg-oxides
- Banded iron formation = 10 - 80%  $\text{Fe}_2\text{O}_3$ , remainder  $\text{SiO}_2$
- Dolomite (Ca-Mg carbonate) = 30% CaO, 18% MgO
- Oil-shale = ~28%  $\text{SiO}_2$ , 28%  $\text{C}_{\text{TOT}}$ , Al-, Ca-, Fe-, alkali-oxides

# Sample Preparation

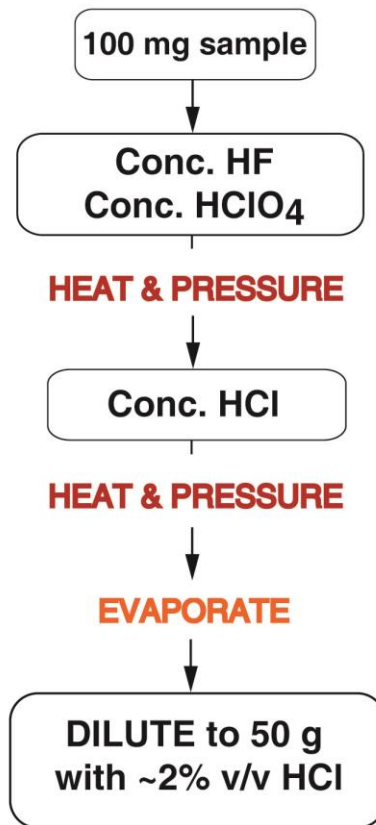
## 2 sample preparation methods:

- High P/T HClO<sub>4</sub>-HF
- Low T HNO<sub>3</sub>

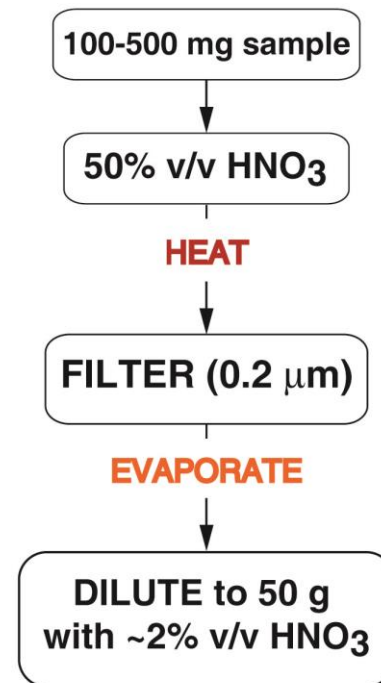
Spike recoveries 97-99%

Dilution factors – 250 to 5000x

### HF-HClO<sub>4</sub> PRESSURE DIGESTION



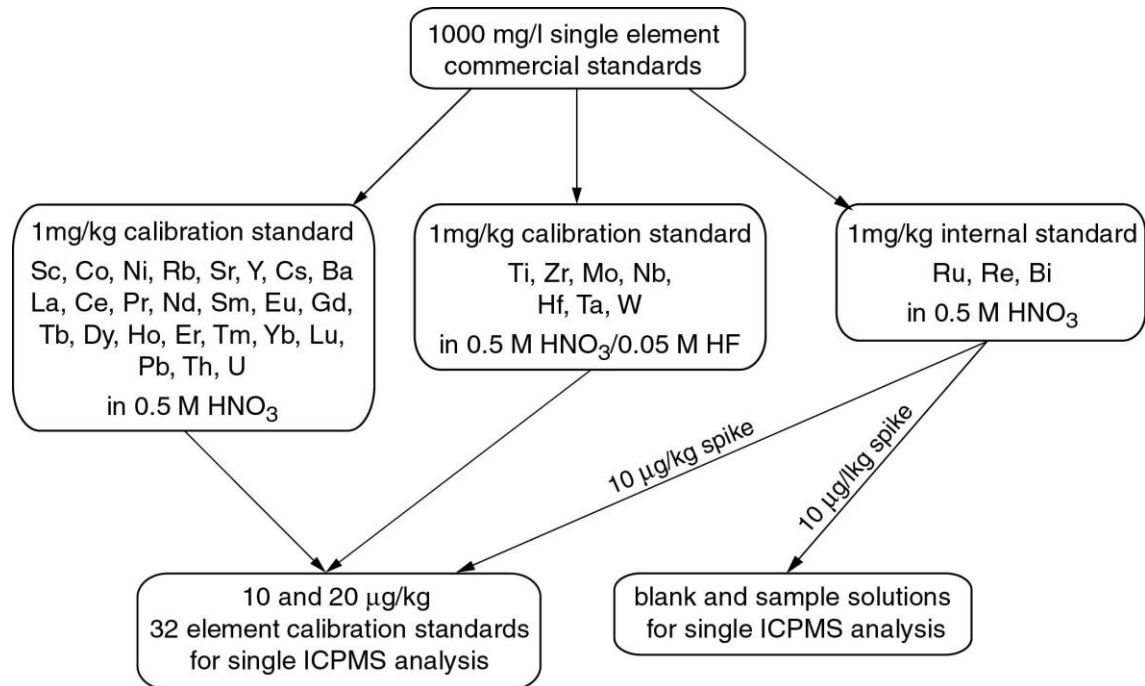
### HNO<sub>3</sub> OPEN DIGESTION



# Standards and Calibration

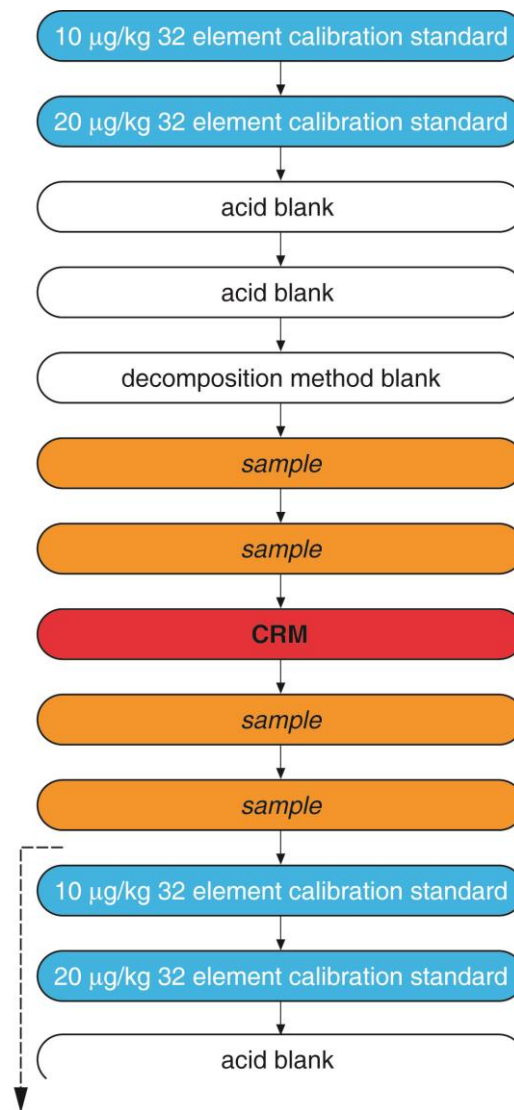
## Multi-element standards prepared gravimetrically

- $\text{HNO}_3$  or  $\text{HCl}$  final matrices
- Ru, Re, Bi internal standards



# Sample Measurement

- Standard bracketing
- Multiple blanks (acid and method)
- No data manipulation by ICP-MS software





# Data Reduction

**All data reduced offline (spreadsheet)**

## **Order of Corrections**

- 1) Internal Standard Correction
- 2) Interference Corrections (primarily  $MO^+$  for rare earths)
- 3) Blank Correction

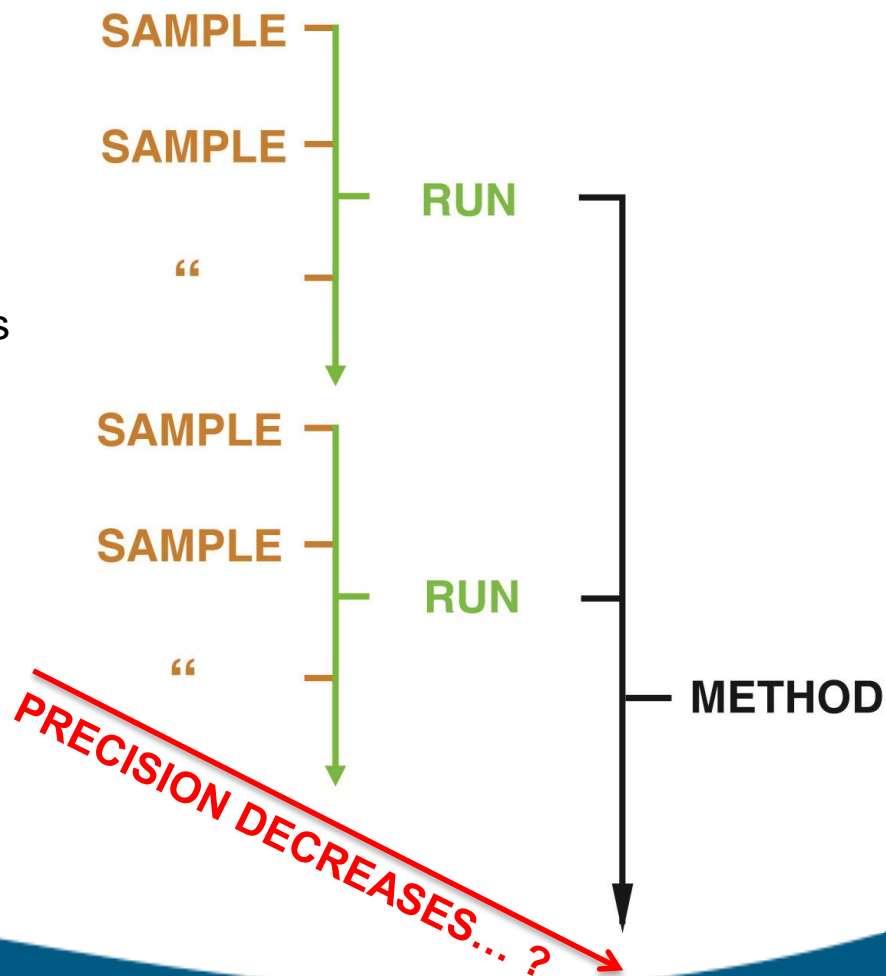
# Measures of Precision

**SAMPLE PRECISION** – scans of single analytical solution

**RUN PRECISION** – multiple measurements of single analytical solution in one day

**METHOD PRECISION** – multiple preparations and measurements of rock powder over time (weeks to years)

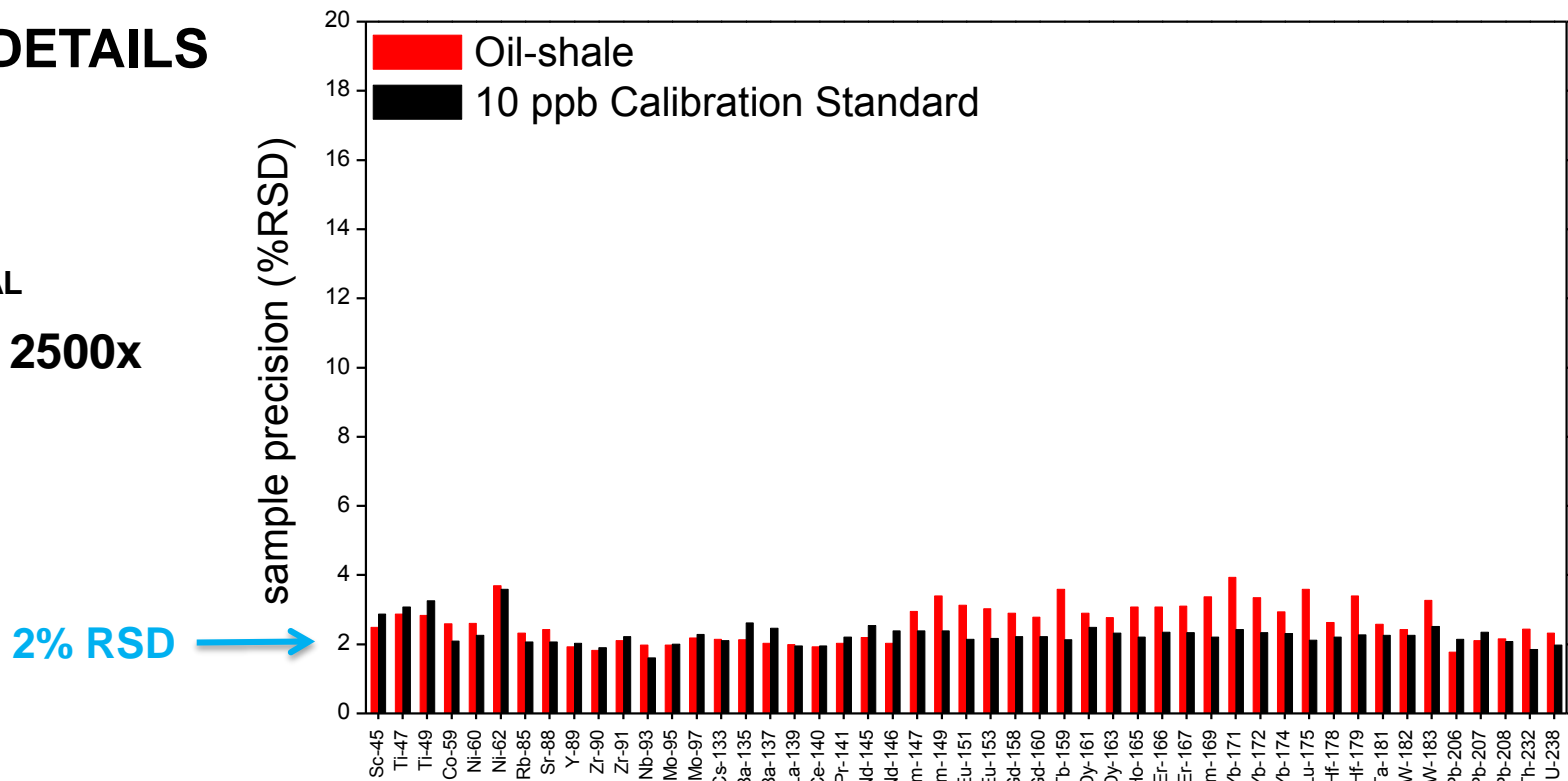
**ALL DATA as %RSD**



# Sample matrix effect

## SAMPLE DETAILS

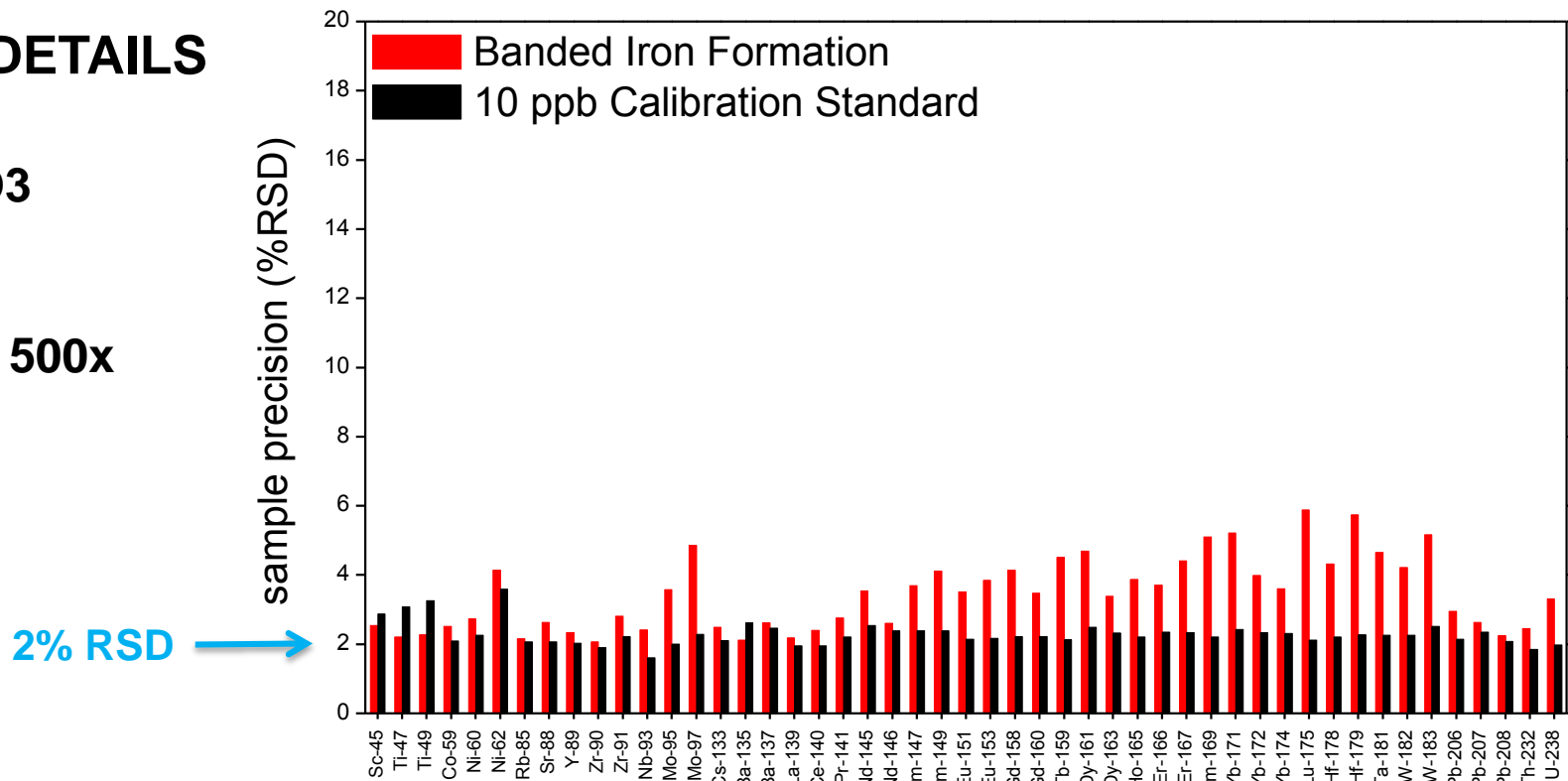
- 28% SiO<sub>2</sub>
- 28% C<sub>TOTAL</sub>
- Dilution = 2500x



# Sample matrix effect

## SAMPLE DETAILS

- 40% Fe<sub>2</sub>O<sub>3</sub>
- 50% SiO<sub>2</sub>
- Dilution = 500x

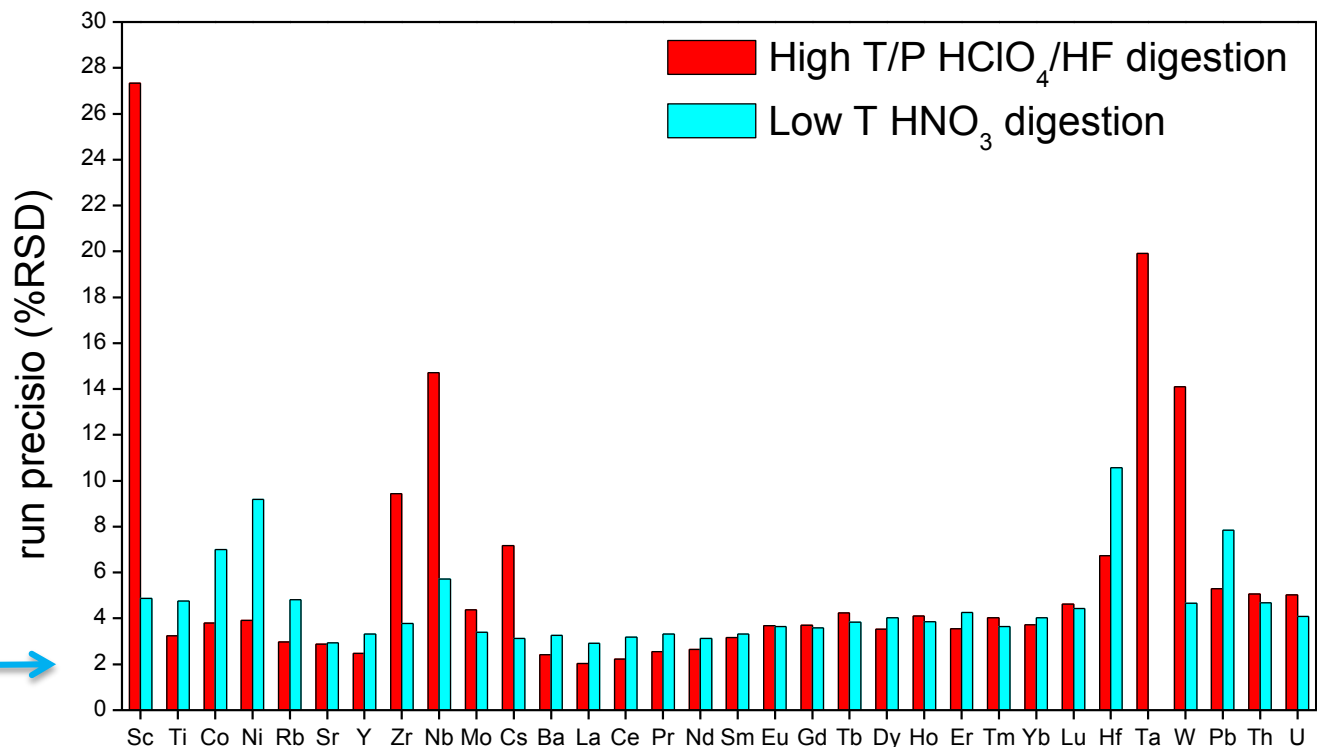


# Decomposition method effect

## SAMPLE DETAILS

- Ca-Mg carbonate
- 30% CaO, 18% MgO
- Dilution = 500x

2% RSD →

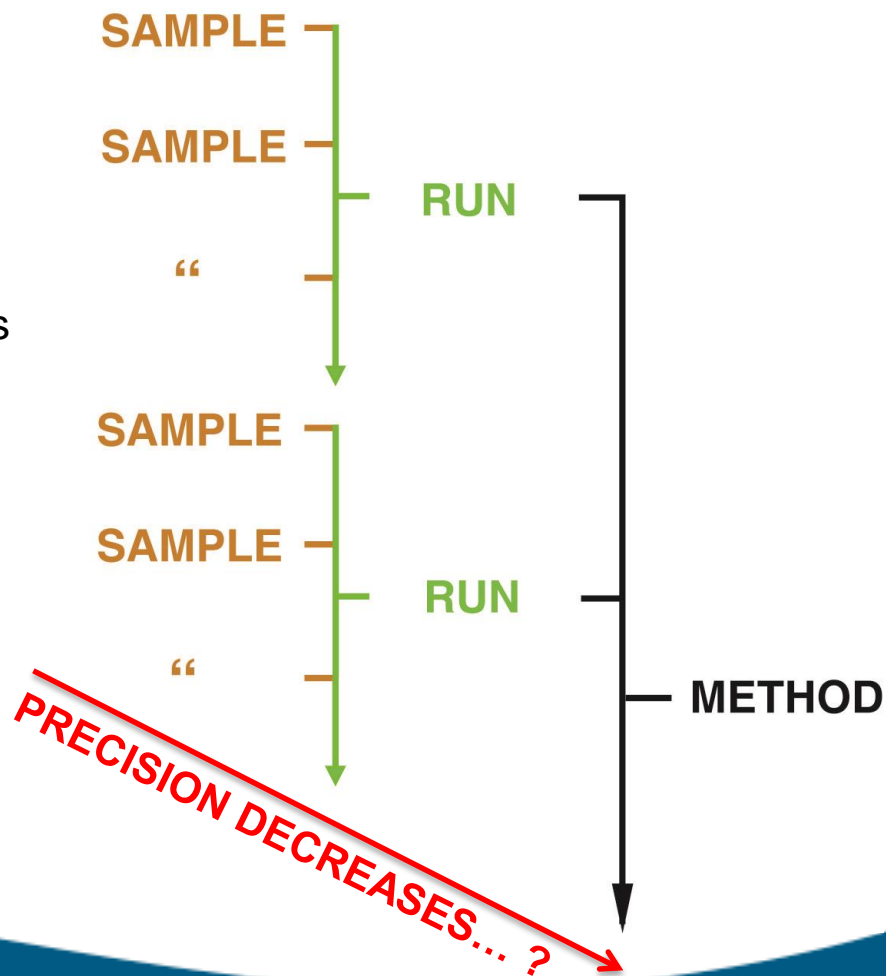


# Measures of Precision

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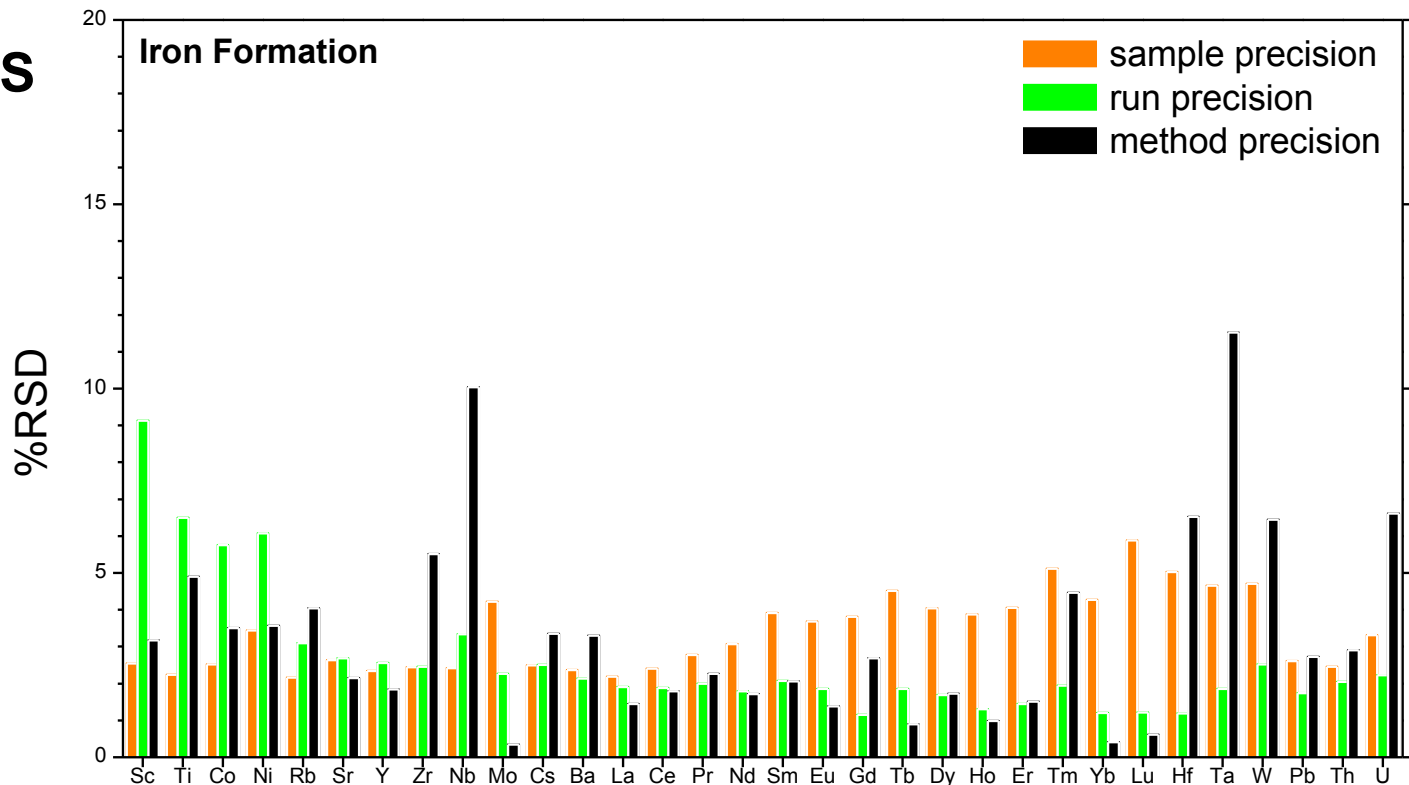
# Comparison of different measures of precision

## SAMPLE DETAILS

- 40% Fe<sub>2</sub>O<sub>3</sub>

- 50% SiO<sub>2</sub>

- Dilution = 500x



# Comparison of different measures of precision

## SAMPLE DETAILS

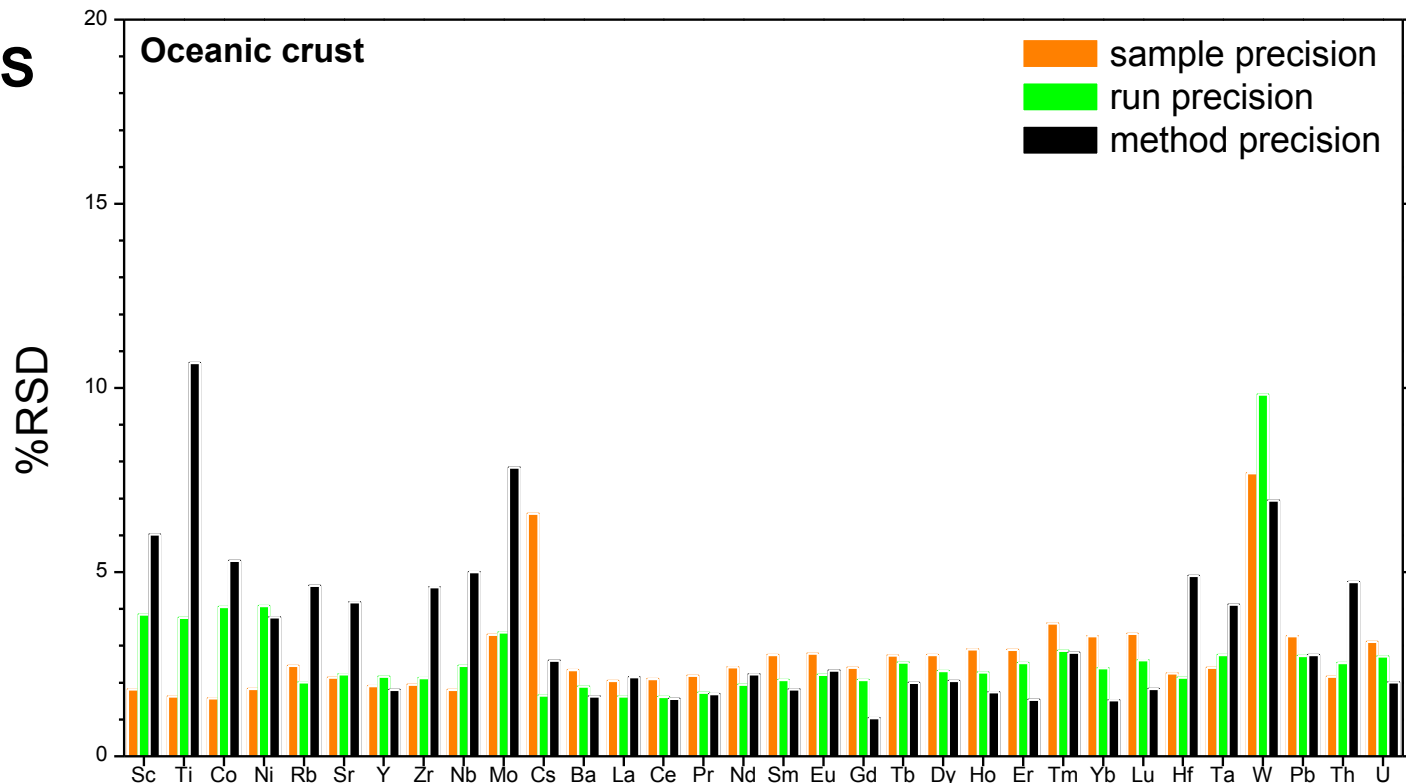
- 50% SiO<sub>2</sub>

- 13% Fe<sub>2</sub>O<sub>3</sub>

- 13% Al<sub>2</sub>O<sub>3</sub>

- 7% MgO

Dilution = 2500x





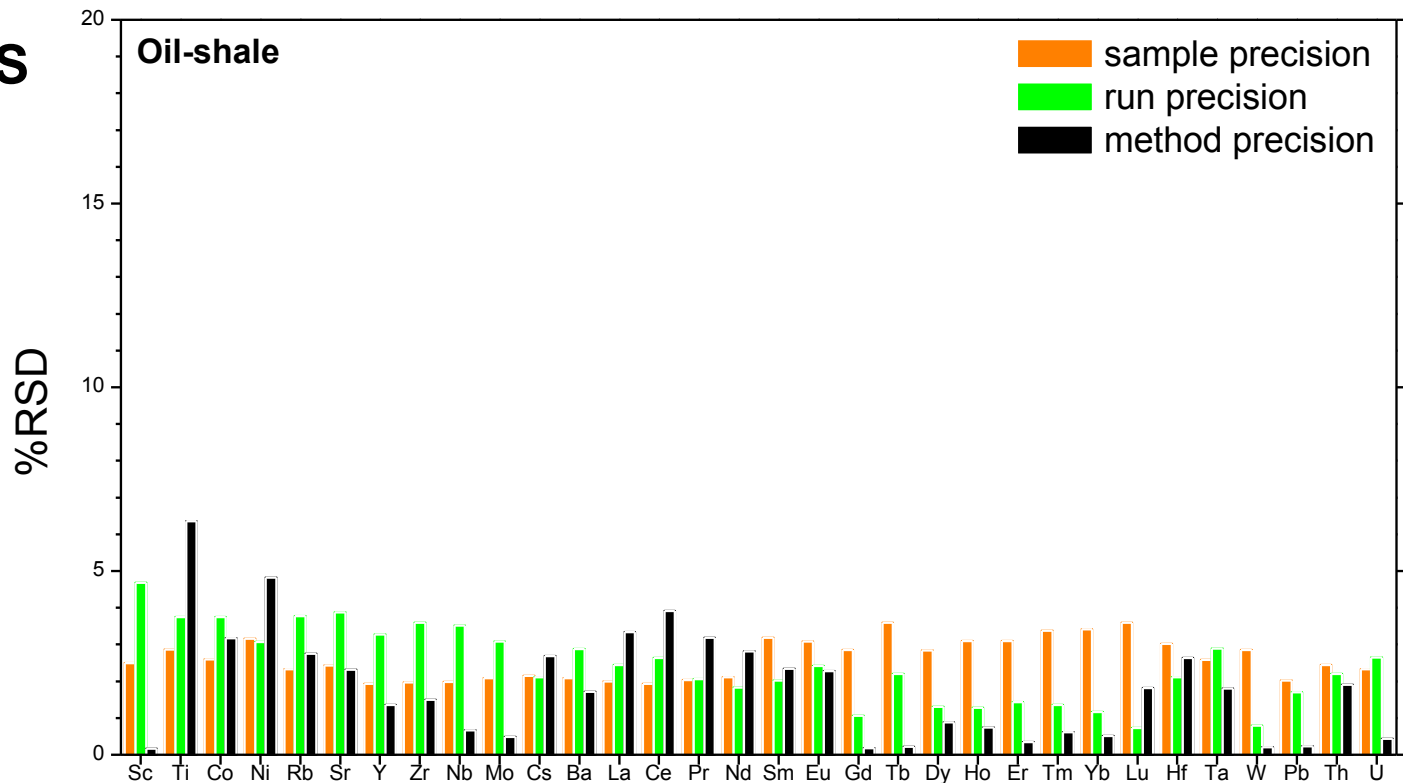
# Comparison of different measures of precision

## SAMPLE DETAILS

- 28% SiO<sub>2</sub>

- 28% C<sub>TOTAL</sub>

- Dilution = 2500x



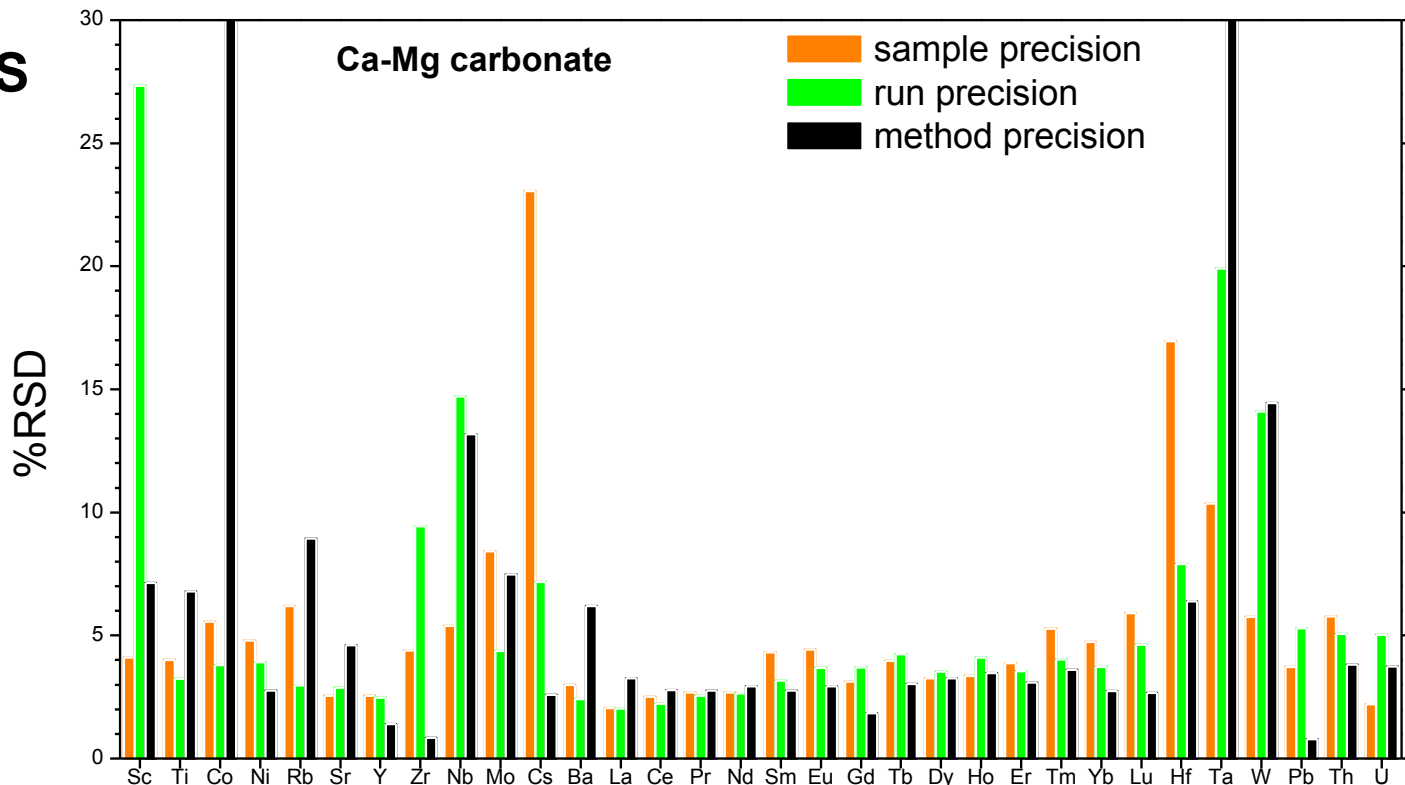
# Comparison of different measures of precision

## SAMPLE DETAILS

- 30% CaO

- 18% MgO

- Dilution = 500x



# Ca & Mg effect on Co

Ca-Mg carbonate RM

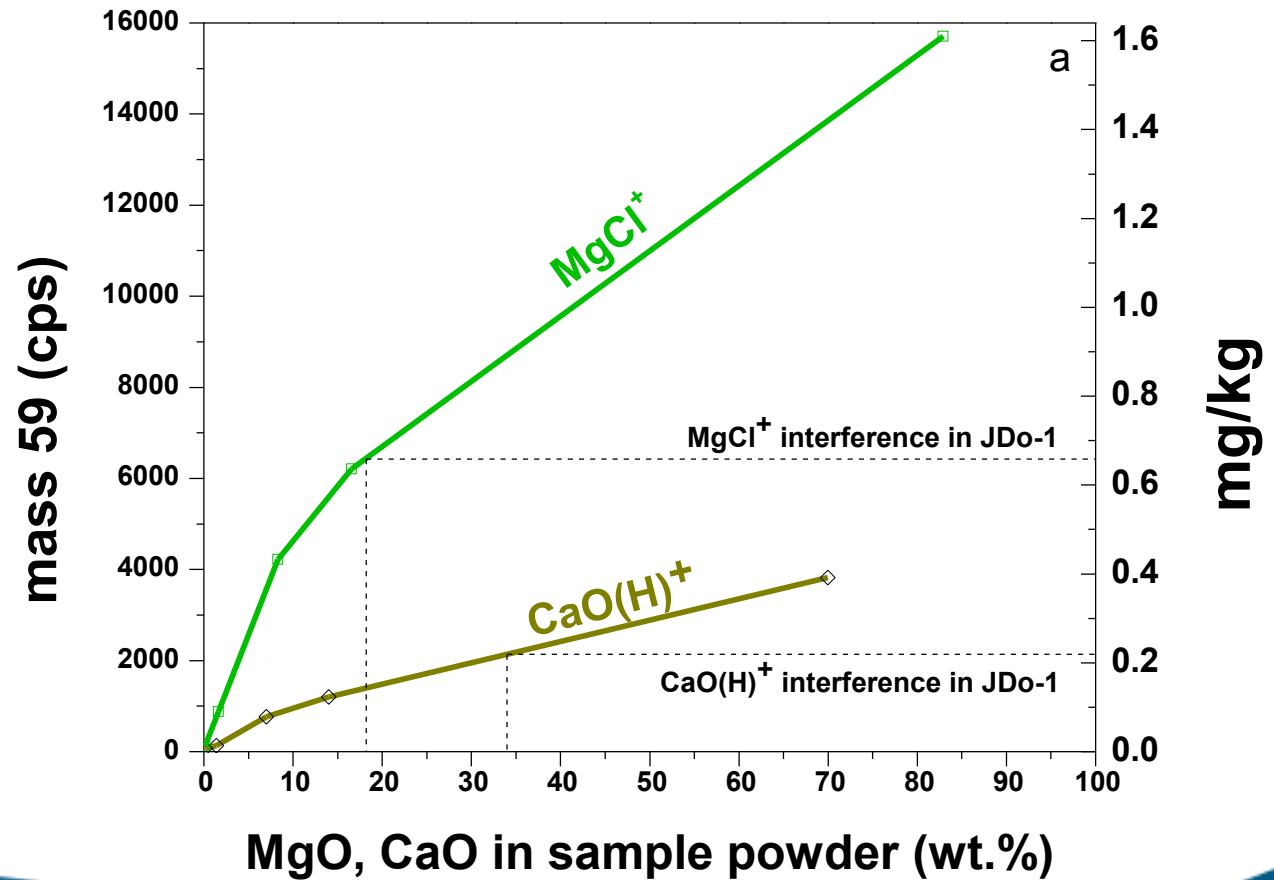
- 30% CaO

- 18% MgO

- Dilution = 500x

Literature values:

Co ~0.2 ppm



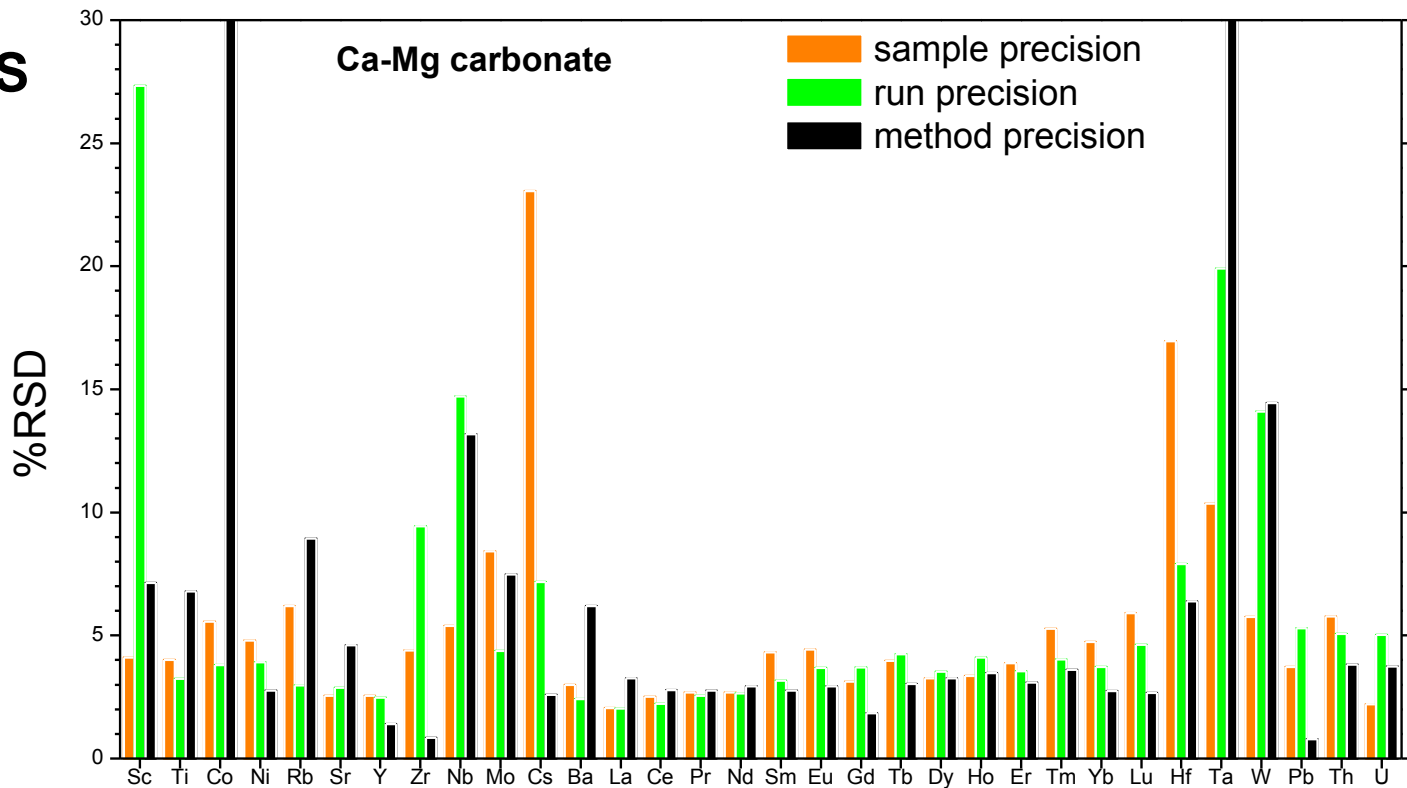
# Comparison of different measures of precision

## SAMPLE DETAILS

- 30% CaO

- 18% MgO

- Dilution = 500x



# Observations

- Results are accurate, and where not, explainable
  - Solutions prepared gravimetrically!
- ICPMS (machine) %RSD significant
- Human factor (sample prep) generally not controlling precision for many elements
- Sample introduction system simple (robust)
  - Different sample intro systems can improve precision